Chapter 6

Synthesis & characterization of silica NPs from bamboo leaves and its application as a support for TiO_2 NPs to enhance photocatalytic degradation of dye.

Nanoparticles of silica due to their chemically inert nature, high surface areas, UV transparency and great physical stability act as one of the best support materials. In this chapter, silica nanoparticles are synthesized from a green source, i.e., *Bambusa bambos* (bamboo) leaf through thermal combustion and precipitation technique. Obtained nanoparticles are employed along with TiO_2 nanoparticles to enhance the photo catalytic degradation of methylene blue dye. Nearly spherical nanoparticles with average particle size in the range 15-25 nm and 20-50 nm with a BET surface area of $250 m^2g^{-1}$ and $194 m^2g^{-1}$ are obtained at 0.5 M NaOH and 1 M NaOH respectively. X-Ray diffraction results confirmed the synthesis of pure amorphous SiO_2 nanoparticles. Dye degradation studies reveal that, addition of SiO_2 nanoparticles along with TiO_2 nanoparticles in the 1:4 ratio has improved the degradation from 88.9 % to 94.66 %. Study also reveals that the dye degradation follows a pseudo first order kinetic model.

6.1 Introduction

Despite such excellent properties of TiO_2 as discussed in Chapter 3, 4 & 5 there are certain problems associated with nanometric TiO_2, which make practical applications difficult and costly. A great deal of research has been carried out to improve the photocatalytic properties of TiO_2 by using a solid support with a primary objective of achieving more active sites per unit area, consequently, a higher photocatalytic reaction rate. Anderson and Bard (1997) suggests that, in the photocatalytic process employing

mixed oxides of silica-titania, the substrate adsorption step assumes great relevance. It is suggested that the presence of SiO_2 promotes the substrate pre-concentration on the surface of the material, which results in higher accessibility to photo-excited TiO_2 present on the surface of the photo catalyst (Anderson and Bard, 1997). Similarly, the anatase to rutile transformation is suppressed if TiO_2 is immobilized on silica (Li et al., 2013). Several researchers used SiO_2 nanoparticle to reduce the recombination of photo generated electron-hole pair and to increase the surface area of the TiO_2 photo catalyst for the purpose of improving the photo degradation ability of dyes (Li et al., 2013; Li et al., 2008). Silica was considered to be one of the best supports for accommodating nano photo catalysts because they are chemically inert, possess high surface areas, are transparent to UV radiation and have great physical stability (Cordoba et al., 2019). These features make silica an ideal material for many applications as synthetic adsorption materials (Jang et al., 2009, Lakshmi et al., 2009, Wongjunda et al., 2010), fillers in composite materials, carriers, and medical additives (Liu et al., 2005, Shin et al., 2008).

Generally, some chemicals like tetraethylorthosilicate (Kim et al., 2002) and tetramethoxysilane (TMOS) (Niki et al., 2009) are widely used as the silica source to synthesize silica nanoparticles. But these chemical are relatively expensive and toxic in nature and are harmful to environment (Amutha et al., 2010). Thus nanoparticle synthesis route should be economical, cost-effective, non-toxic and productive. Rice husk ash (RHA) is one of the most silica-rich raw materials containing about 90% to 98% silica (Abu Bakar et al., 2010, Krishnarao et al., 2001, Real et al., 2008). Next, to rice husk, bamboo leaf ash contains more than 70% amorphous silica in it with high surface area.

Various methods have been used to synthesis silica nanoparticle from bio-waste like, sol-gel method with an average dimension of 80 nm (Amutha et al., 2010, Liou et al., 2011), precipitation method with particle size of 5–10 nm (Nittaya et al., 2008), and dissolution and precipitation method with particle sizes of 5-30 nm (Liou et al., 2011). In comparison to these techniques, thermal combustion and precipitation technique holds advantage of use of cheap and easily available chemicals like hydrochloric acid, sulfuric acid and sodium hydroxide. Also, biomass can used as silica source in this synthesis technique.

In this chapter, silica nanoparticles are synthesized from bamboo leaves using thermal combustion and precipitation technique. Structure and morphology of the synthesized particles is confirmed with the help of various characterization techniques i.e. XRD, SEM-EDX, BET, DLS, and FTIR. SiO_2 particles along with the TiO_2 NPs are used to enhance the photocatalytic degradation of methylene blue dye.

6.2 Experimental

6.2.1 Materials

The leaves of bamboo species named *Bambusa bambos* are collected from the campus of BHU, Varanasi, Uttar Pradesh, India. Sodium Hydroxide procured from Sisco Research Laboratories Pvt. Ltd.(AR, 98%) , Hydrochloric Acid LR (37%, Central Drug House (P) Ltd., India), Sulfuric Acid AR(98%, Central Drug House (P) Ltd., India.) Milli-Q water (18.2ohm**)** is prepared in the laboratory of the Chemical Engineering Department, IIT (BHU) Varanasi.

6.2.2 (A) Synthesis of SiO_2 nanoparticles

Bamboo leaves collected from the campus are thoroughly cleaned to remove any sand and dust particles accommodated on the surface. After that the leaves are allowed to dry for sufficient time and further ground to powder form for use. Powdered leaves are further acid leached by HCl (10% v/v) solution and the resultant powder is heated in the muffle furnace at 950°C for 6 h. Obtained Bamboo Leaf Ash (BLA) post furnace treatment is mixed with NaOH solutions with varying concentrations from 0.1M to 1.0M as shown in the Table 6.1 while continuous stirring the samples at a temperature range of 60°C to 100°C as given in the Table 6.2 for a period of 4h. Main parameters which influence the synthesis of the SiO_2 are optimised by varying one parameter keeping other constant as shown in the Table 6.1 and Table 6.2 . The solution is filtered, and collected filtrate is titrated with 10% v/v H_2SO_4 until the pH of the solution reaches 7 under vigorous stirring for overnight. Formed gel is filtered with filter paper (Whatman filter paper, Grade 42) and washed with distilled water. Afterward, it is dried in an oven for 8 hours at 70°C. Finally, it is calcinated for 6 hours at 650°C in a furnace. Reactions involving the synthesis process are mentioned in equation (6.1 to 6.4) and the synthesis procedure is shown in Figure 6.1.

Bamboo Leaves Ash (BLA) + HCl $\rightarrow$ Metal impurities (Leaching) (6.1)

$BLA + 4NaOH \rightarrow 2Na_2SiO_3 + 2H_2O$ (Alkali extraction) (6.2)

$2Na_2SiO_3 + 2H_2SO_4 \rightarrow Si(OH)_4 + Na_2SO_4$ (Acid precipitation) (6.3)

$Si(OH)_4 \rightarrow$ Drying $\rightarrow$ Calcination$\rightarrow SiO_2 + 2H_2O$ (6.4)

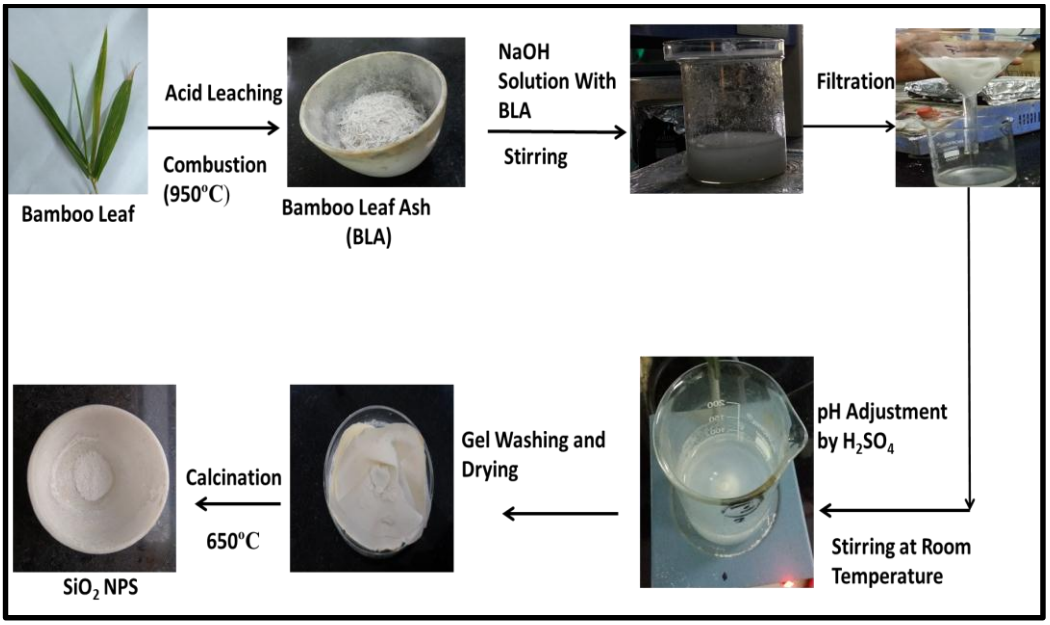

Figure 6.1 Synthesis processes of SiO_2 nanoparticles from bamboo leaf

Table 6.1 SiO_2 synthesis with NaOH concentration variation

Bamboo Leaf Ash(g)	**NaOH**	**Temperature (°C)**	**H_2SO_4**
2.5	0.1M	**100**	10M
2.5	0.5M	**100**	10M
2.5	1.0M	**100**	10M

Table 6.2 SiO_2 synthesis with temperature variation

Bamboo Leaf Ash (g)	**NaOH**	**Temperature (°C)**	**H_2SO_4**
2.5	0.5M	60	10M
2.5	0.5M	80	10M
2.5	0.5M	**100**	10M

6.2.2 (B) Synthesis of SiO_2 / TiO_2 /PDMS film

For the synthesis of polymeric matrix embedded with TiO_2/ SiO_2NPs, the same method is followed as discussed in chapter 5. Base polymer poly dimethyl-siloxane (PDMS) crosslinking agent tetraethyl-ortho-silicate (TEOS), catalyst dibutyltin dilaurate and organic solvent (Toluene) are taken in a weight ratio of 1:0.2: 0.07: 4. Steps involved in the synthesis of polymeric film with nanoparticles (SiO_2, TiO_2) are almost same, except the addition of SiO_2 nanoparticles in the ratio 1:4 (SiO_2:TiO_2). This optimal value of SiO_2 addition is considered based on various research works mentioned in the literature (Mahesh et al., 2014, Pakdel et al., 2018). Schematic representation of synthesis procedure for SiO_2 / TiO_2 /PDMS film is shown in Figure 6.2.

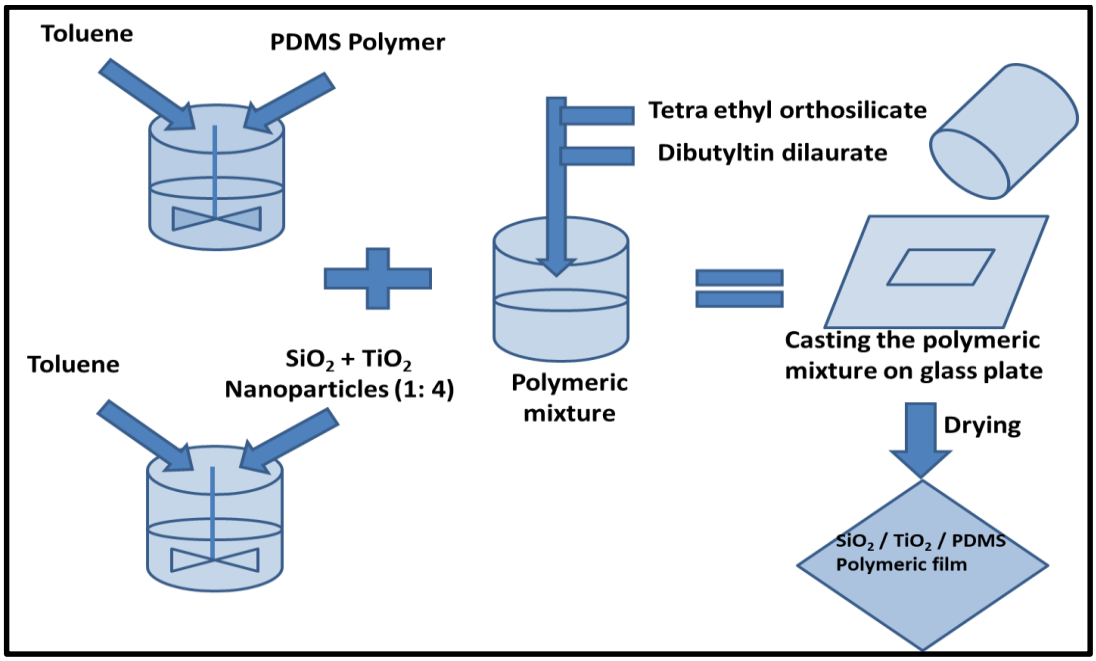

Figure 6.2 Immobilization of nanoparticles on PDMS polymer

6.2.3 Characterization Techniques

Morphological structure and distribution of synthesized SiO_2 nanoparticles are analyzed by high-resolution scanning electron microscopy (HRSEM) (Nova Nano SEM 450)

equipped with an energy dispersive X-ray spectroscopy system (EDX Inc.). The X-ray diffraction (XRD) patterns of the samples are measured at room temperature using Ultima IV, Rigaku X-ray diffractometer (Cu-K$\alpha\lambda$= 0.154 nm) radiation under 40 kV / 15 mA within a 2θ range of 10°–80°. N_2 adsorption desorption isotherms are obtained with an ASAP 2020, Micromeritics apparatus. Fourier transfer infrared spectrometer (Model Nicolet 560) is utilized for FT-IR characterization in KBr pellets. Average particle size analysis is performed by a dynamic light scattering unit (DLS, Nano plus common). Concentrations of dyes are determined using an UV-vis spectrophotometer (Systronic 2202).

6.3 Results and Discussion

6.3.1 Variation in Parameter (Temperature, NaOH concentration)

Mainly two parameters (temperature & NaOH concentration) are taken into consideration for the synthesis of the SiO_2 NPs because both the parameters are mainly responsible for the extraction and formation of nanosilica from the biomass. When the reaction temperature is operated at 60°C keeping NaOH concentration as 0.5N, no precipitation occurred in the form of gel. But as the temperature is increased from 60°C to 100°C, more silicate ions form in solution mixture. As a result more silica is recovered from the bamboo leaves ash in the form of gel which later upon drying and calcination resulted in the formation of desired SiO_2 NPs. So, in this experiment 100°C temperature is taken as the reaction temperature for synthesis of SiO_2 NPs.

Effect of NaOH concentration on the synthesis process by taking experimental condition as given in the Table 6.1 is performed. At low concentration of NaOH (0.1M), no precipitation is observed, but as the NaOH concentration is increased to 0.5M and

1.0M, a good amount of gel is formed. The yield percentage of SiO_2 NPs is 59.6% and 55.6% with 1.0M and 0.5M NaOH concentration respectively at the temperature of 100°C. However, the size and surface area of the synthesized particles will also be considered to decide the required product for usage.

6.3.2 XRD Analysis

XRD diffractograms of synthesized nanosilica showed broad peaks at $22° \leq 2\theta \leq 23°$ as shown in the Figure 6.3. At both the NaOH concentrations (1M, 0.5M), presence of single broad peak and absence of any other sharp peaks indicates the amorphous nature of synthesized SiO_2 NPs and also confirms the absence of impurities in the synthesized particles (Chen et al., 2014, Liou and Yang, 2011).

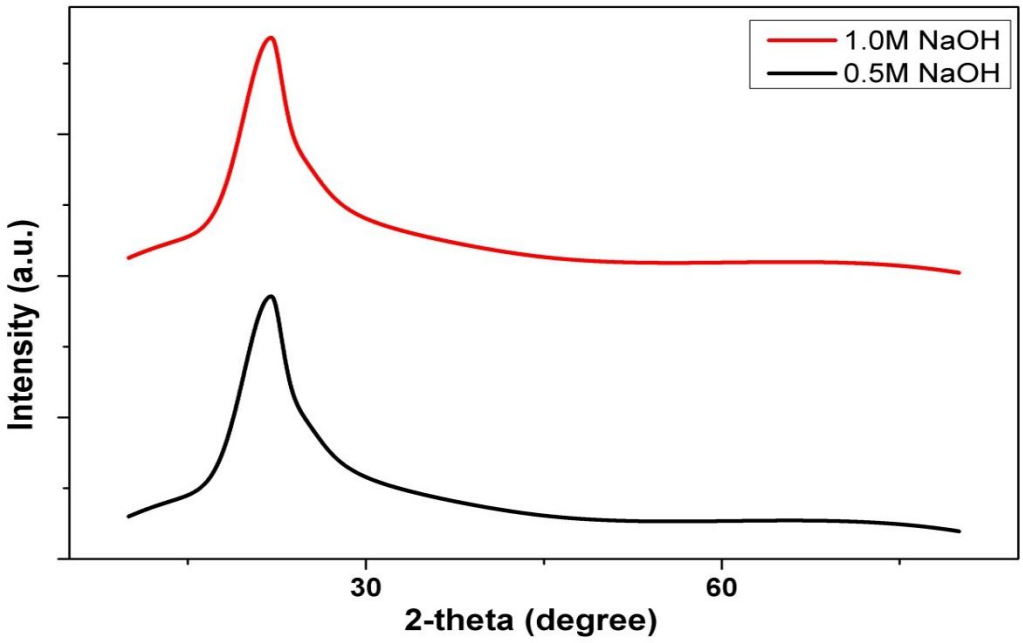

Figure 6.3 X-Ray diffraction patterns of SiO_2nanoparticles at different NaOH concentration

6.3.3 FTIR Analysis

Fourier transform infra-red Spectroscopy of SiO_2NPs provides information about specific functional groups present in the prepared SiO_2NPs which examines the sample purity. The peak in Figure 6.4 corresponding to 463 cm^{-1}signifies bending vibrations of Si-O-Si part. The peak at 802cm^{-1}shows the presence of Si-O bending vibrations (Hernandez et al., 2000).The broad peak at 1089cm^{-1} represents the asymmetric (Si-O-Si) elongating vibration signifying arrangement of the bonding structure of O and Si atoms (Moncada et al., 2007). Broad peak at 3023 cm^{-1} is due to the Si -OH groups and absorbed water (Soria et al., 2010). The characteristic of FTIR graph and position of peaks for 0.5M and 1.0 M NaOH samples is found to be identical. Thus, FTIR analysis further validates the successful formation of SiO_2NPs.

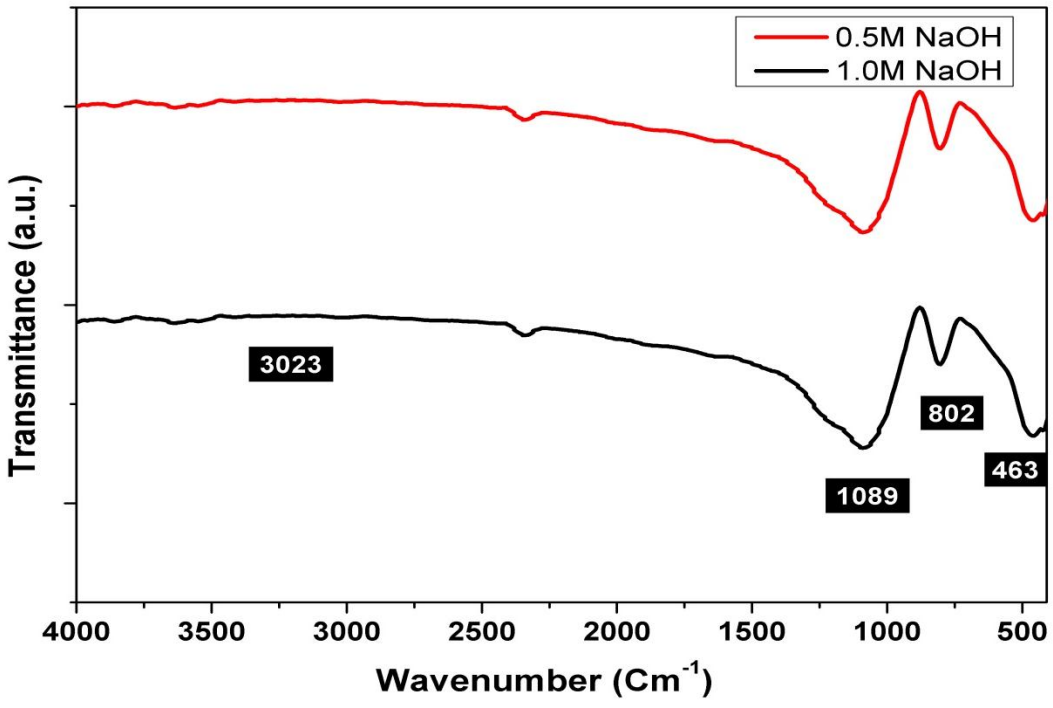

Figure 6.4 FTIR spectra of synthesized SiO_2 nanoparticles at different NaOH concentration

6.3.4 SEM - EDAX Analysis

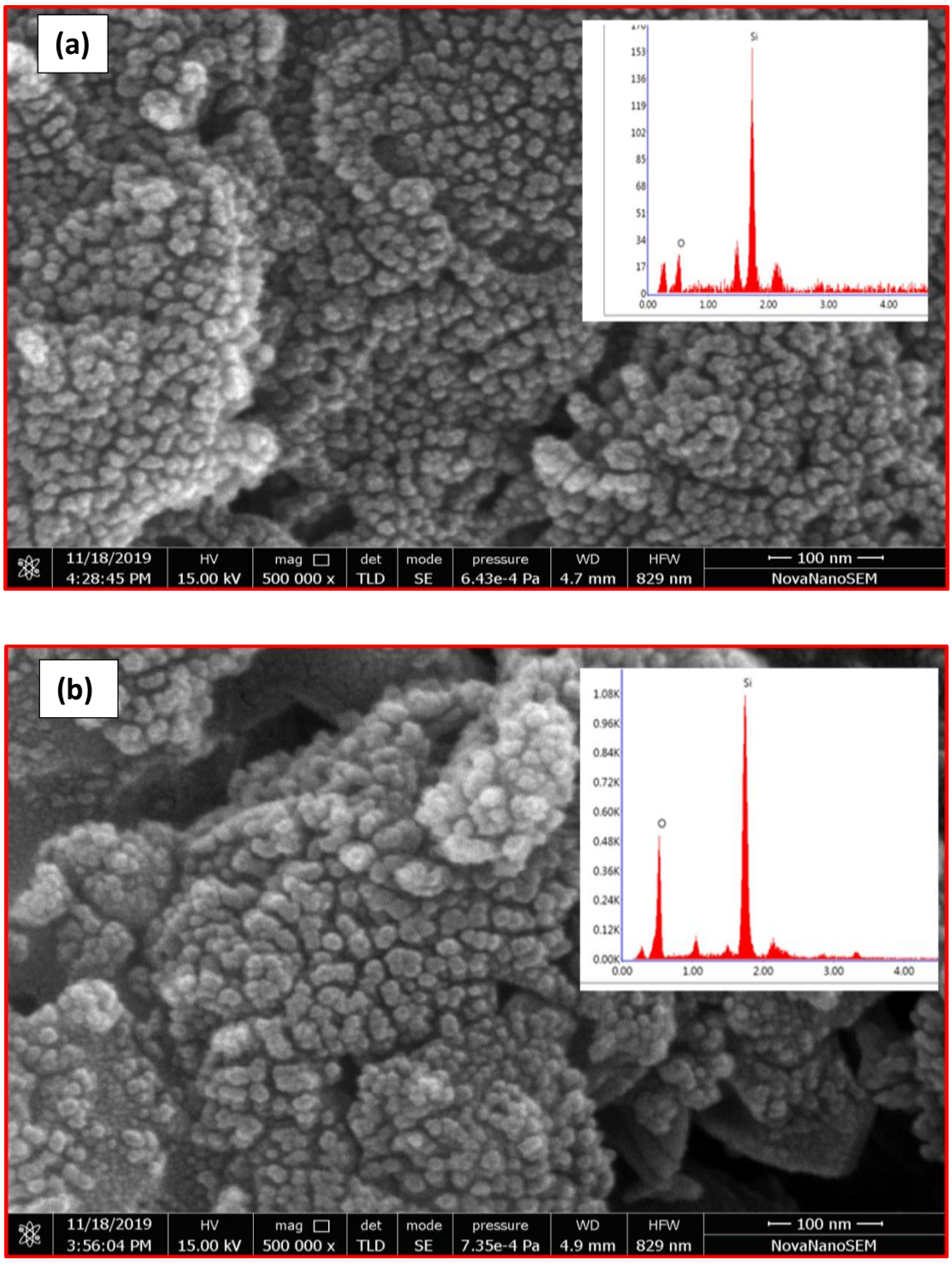

Figure 6.5 HRSEM-EDAX image of synthesized SiO_2 nanoparticles at (a) 0.5M NaOH (b) 1.0M NaOH

The HRSEM analysis is performed to determine the average grain size and shape of the synthesized SiO_2NPs. The HRSEM image evidence the formation of spherical shaped SiO_2 NPs with a diameter in the range of 15 nm to 25nm as shown in the Figure 6.5(a) with 0.5M NaOH. It is also visible in the image that small and distinct SiO_2NPs are observed along with few large sized agglomerated nanoparticles. But in the Figure 6.5(b), the average sizes of the particles are in the range 20nm to 50nm with 1.0M NaOH for the particle synthesis. In this case particles are bigger in size due to the agglomeration. In both the cases the particle size is nearly same but the agglomeration as well as the NaOH consumption is less for 0.5M NaOH sample. The X-ray Energy Dispersive Spectrometer (EDS) is employed to know the elemental composition of the synthesized SiO_2 NPs. EDAX spectrum as shown in inset of Figure 6.5(a) and Figure 6.5(b), confirms the presence of silica (Si) and oxygen (O) without any impurity in the sample with weight percentage 51.30%, 48.70% and 48.57%, 51.43 for 0.5 M and 1.0 M NaOH respectively.

6.3.5 DLS & BET analysis

Particle size ditribution analysis is done by use of dynamic light scattering principle. Before the analysis, the SiO_2 NPs are dispersed in water followed by ultra-sonication to achieve uniform distribution of nanoparticles in water at neutral pH. The particle size distribution of the synthesized SiO_2 NPs at 0.5M NaOH and 1.0M NaOH concentrations as shown in the Figure 6.6 (a) are in the range 20nm to 100nm and 30nm to 170nm respectively. The average particle size increases due to agglomeration and less spherical shape of the SiO_2 nanoparticle synthesized with increasing concentration of NaOH.

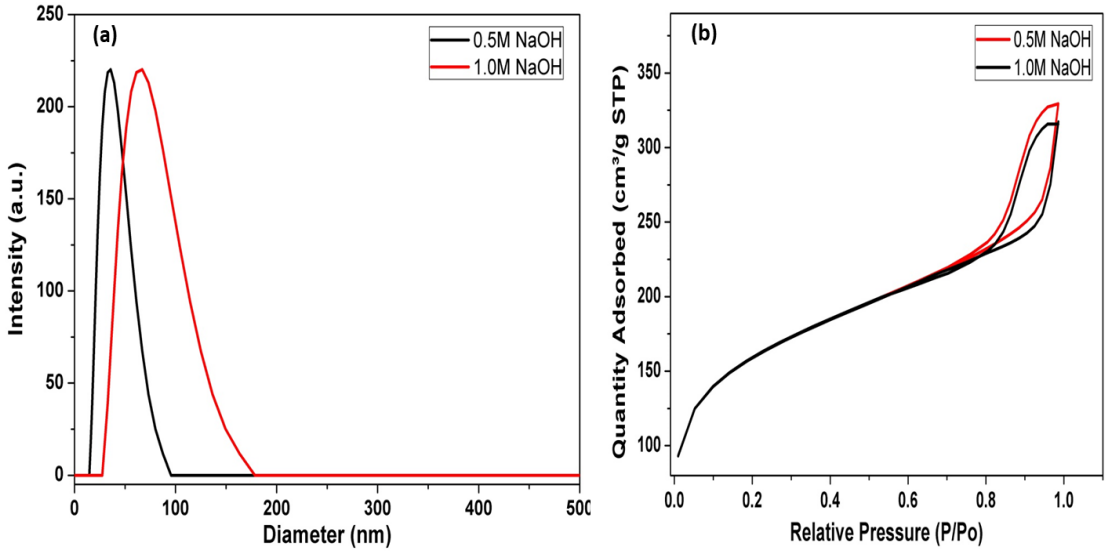

Figure 6.6 (a) Particle size distribution, **(b)** N_2 Adsorption/desorption isotherm of synthesized SiO_2nanoparticles at different NaOH concentration.

BET surface area of the prepared silica nanoparticles is investigated using Brunauer-Emmett-Teller (BET) surface area analyzer (ASAP 2020, Micromeritics) through inert gas (N_2) adsorption-desorption measurements. BET surface areas are found to be 250 m^2/g and 194 m^2/g at 0.5M and 1.0M NaOH concentration and respective plots are shown in Figure 6.6 (b) derived from nitrogen absorption-desorption process. So, from the particle characterization studies, it is confirmed that nanoparticles synthesized with 0.5M concentration NaOH have small particle size with less agglomeration and high surface area which makes it more suitable for the application.

6.3.6 Synthesized particle performance evaluation with TiO_2 NPs for dye degradation

Immobilizing both the nanoparticles in the thin film followed the same path as discussed in the previous chapter (Chapter 5). The amount of SiO_2 and TiO_2 nanoparticle is kept constant by taking 1: 4 ratios and all other conditions are same for

the immobilizing technique. Same photo catalytic reactor is used to conduct the experiments. The photo catalysis experiment is also performed in the same way as done in the previous chapter. The time-dependent UV–Visible spectra of methylene blue (MB) of same concentration (5ppm) are shown in Figure 6.6(a). MB shows a maximum absorption peak at wavelength 665 nm. An inverse relation is observed between the absorbance and the irradiation time. Figure 6.7 (a) depicts that absorption peak of MB declines significantly and maximum degradation within 3 h is achieved in presence of nanocomposite film. The percentage degradation of dye by the usage of nanocomposite film is shown in Figure 6.7 (b) and it was found to be up to 94.66 %.

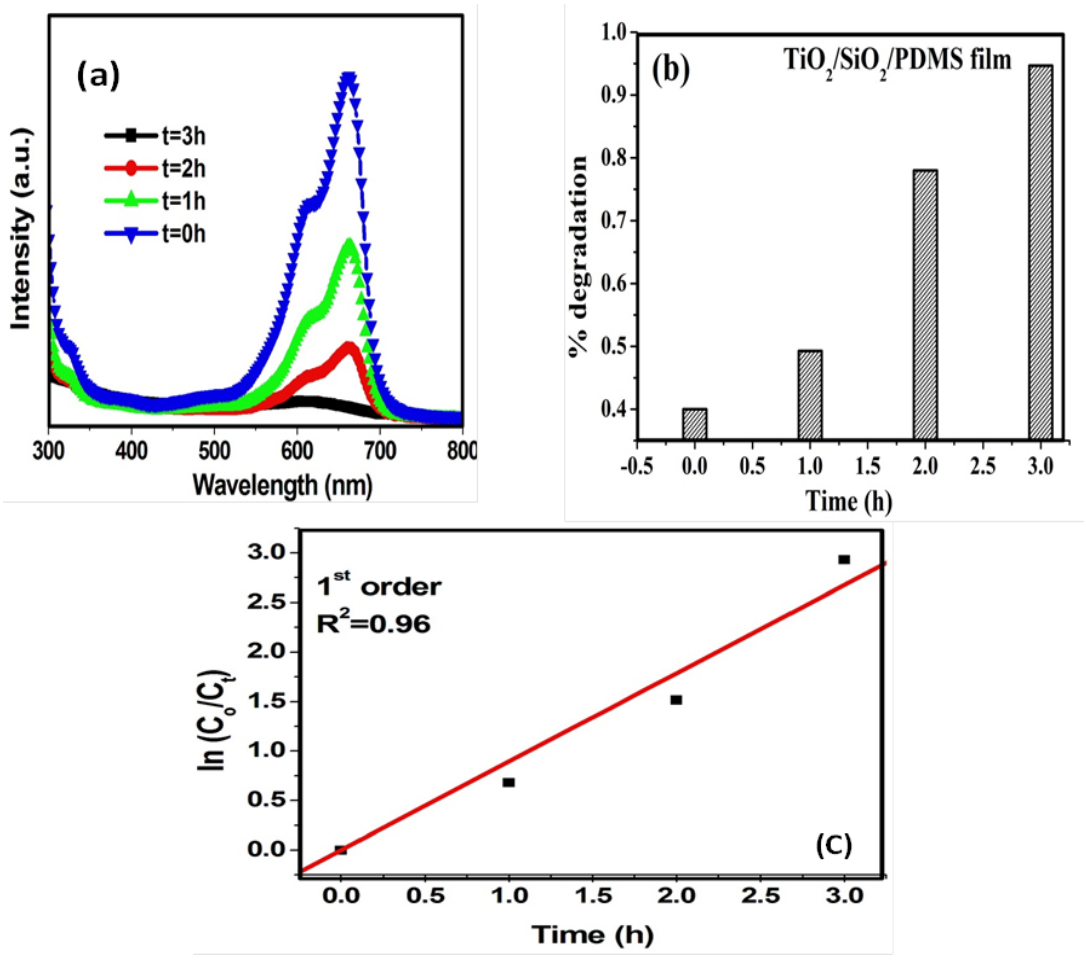

Figure 6.7 (a) UV spectra of MB solution at different time interval, **(b)** MB degradation versus time **(c)** plots for pseudo-first order in photocatalytic degradation

Pseudo-first order kinetic model is also applied to validate the experimental results and it is shown in the Figure 6.7 (c). Also, the dye concentration degradation obeys a linear pattern and experimental result is justified with the value of R^2> 0.95 and rate constant value is 0.892 h^{-1}.

6.3.7 Reusability of TiO_2/SiO_2/PDMS film

Stability and reusability are important properties to ensure favorable removal of pollutant along with cost effective and environmentally friendly measures (Hu et al., 2016). Here, the degradation of MB (5 ppm) was performed eight times using TiO_2/SiO_2/PDMS film. After each run the film was washed with distilled water for 1 h to remove the residual products and is reused under the same conditions, to evaluate its stability and reusability. As observed in the Figure 6.8, there is a slight decline in the catalytic activity under reuse when compared to the fresh film. However, it is evident that the immobilized TiO_2/SiO_2/ PDMS film showcased good structural stability, excellent performance for reusability making it quite acceptable for treatment of wastewater.

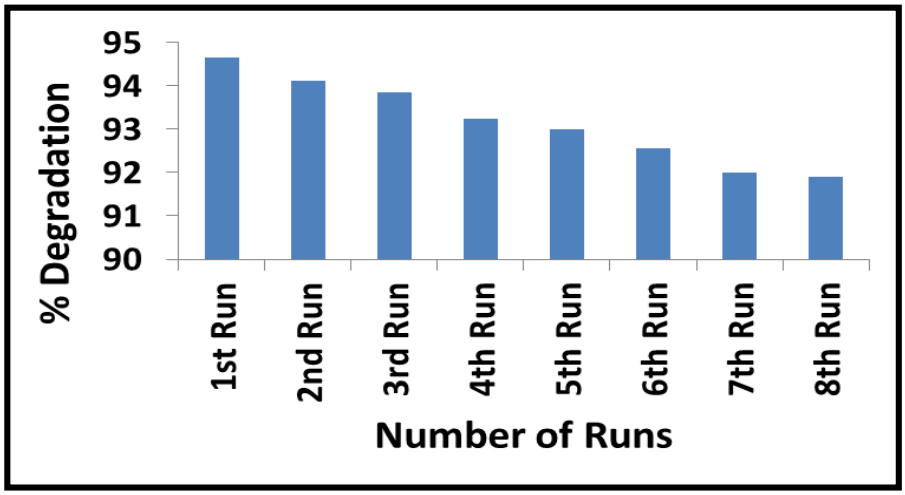

Figure 6.8 Reusability of immobilized TiO_2/SiO_2/PDMS Film

6.4 Conclusion

Amorphous SiO_2 nanoparticles are successfully prepared from Bamboo Leaf Ash by alkali extraction with NaOH followed by acid precipitation with H_2SO_4. Nearly spherical and amorphous nanoparticles with very high specific surface area of $250 m^2 g^{-1}$ with overall particle size distribution in the range of 20-100 nm and average particle size in the range of 15 to 25 nm are synthesized by taking 0.5M NaOH at 100°C. Presence of Si-O-Si, Si-OH and Si-O bonds are also visible in the synthesized SiO_2NP. Synthesized SiO_2 NPs along with the TiO_2NPs are used for photocatalytic degradation of methylene blue dye. Degradation studies showcased a significant improvement in percentage degradation with 94.66 %, which is about 88.9 % without SiO_2 NP's addition. This increase in degradation due to SiO_2 NP addition is inferred due to its high surface area which facilitates improved accessibility of dye towards the photo-excited TiO_2 nanoparticles. Dye degradation followed a pseudo first order kinetics. Thus, SiO_2 NP synthesized using bamboo leaf source not only benefited the dye degradation but also laid a path towards minimization, utilization and value addition of bio-waste.